

METHODS OF PREPARING HIGH ORIENTATION
NANOPARTICLE-CONTAINING SHEETS AND FILMS USING
IONIC LIQUIDS, AND THE SHEETS AND FILMS PRODUCED
THEREBY

5 This application claims priority to U.S. Utility Application No. 11/139,690, filed on May 31, 2005. The aforementioned application is herein incorporated by this reference in its entirety.

FIELD

10 The disclosure generally relates to the use of ionic liquids as a medium for preparing sheets and films of a resin material containing nanoparticles, wherein the nanoparticles are highly oriented within the sheet or film.

BACKGROUND

15 The production of nanomaterials typically requires energy intensive processes. Particular difficulty has been met when attempting to capture nanoparticles and prevent their agglomeration, and then aligning these nanoparticles to produce an orderly array. This can often be attributed to the importance of Brownian motion and surface forces in the nanoscale world. These forces can be significant factors causing agglomeration, such as when strong surface forces make the moving parts of a NEMS device stick together and seize up.

20 A particularly desired oriented nanomaterial is a sheet or film made from a resin material, such as cellulose, in which aligned nanoscale magnetic particles are embedded. Such materials can be used as "smart paper" and in magnetic information storage media. While it is well established that the storage capacity of recording media can be significantly increased by further reducing the grain size and distribution of magnetic
25 particles in the thin film in order to increase the signal-to-noise ratio of the medium, upon reaching the nanoscale for the magnetic particles, it becomes increasingly difficult to adequately distribute the particles and avoid agglomeration. Further, it is often necessary to increase the magnetic anisotropy of the resulting product in order to guarantee thermal stability of the recorded information.

30 Martin *et al.*, *Phys. Rev. E*, 2000, 61(3), 2818-2830, discloses the production of magnetic, field-structured composites (FSCs) by structuring magnetic particle suspensions in uniaxial or biaxial (*e.g.*, rotating) magnetic fields while polymerizing the

suspending resin. However, since the suspensions are produced by polymerizing the resin in which the magnetic particles are suspended, that process can only be used with systems in which the suspending resin is prepared during the process.

When a magnetic particle suspension containing multidomain particles is exposed to a uniaxial magnetic field, the magnetic dipole moment on the particles will generally increase and align with the applied field. The particles will then migrate under the influence of the dipolar interactions with neighboring particles to form complex chainlike structures. If a magnetic particle suspension is instead exposed to a biaxial (*e.g.*, rotating) magnetic field, the induced dipole moments produce a net attractive interaction in the plane of the field, resulting in formation of a complex sheetlike structure. Similar effects occur when suspensions of dielectric particles are subjected to uniaxial or biaxial electric fields. These materials are known in the art as field-structured composites (FSCs). FSCs can have large anisotropies in properties such as conductivity, permittivity, dielectric breakdown strength, optical transmittance, etc. (Martin *et al.*, *ibid.*)

There is thus a need for a method to reliably produce nanomaterials having aligned nanoparticles contained in the material matrix, while also providing high magnetic anisotropy of the resulting material. The materials and methods disclosed herein meet these and other needs.

SUMMARY

In accordance with the purposes of the disclosed materials, compounds, compositions, articles, and methods, as embodied and broadly described herein, the disclosed subject matter, in one aspect, relates to compounds and compositions and methods for preparing and using such compounds and compositions. In a further aspect, the disclosed subject matter relates to methods for producing nanomaterials, particularly in the form of sheets or films, which have nanoparticles uniformly distributed and embedded therein. These nanomaterials are also disclosed herein. Further, nanomaterials having high magnetic anisotropy, permitting their use in thermally stable information storage media, are disclosed as well as methods for their preparation. A still further aspect relates to thermally stable information storage media having high signal-to-noise ratio and high magnetic anisotropy and methods for making such media.

Additional advantages will be set forth in part in the description that follows, and in part will be obvious from the description, or can be learned by practice of the aspects described below. The advantages described below will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to

be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive.

DETAILED DESCRIPTION

5 The materials, compounds, compositions, articles, and methods described herein can be understood more readily by reference to the following detailed description of specific aspects of the disclosed subject matter and the Examples included therein.

Before the present materials, compounds, compositions, articles, and methods are disclosed and described, it is to be understood that the aspects described below are not limited to specific synthetic methods or specific reagents, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting.

Also, throughout this specification, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which the disclosed matter pertains. The references disclosed are also individually and specifically incorporated by reference herein for the material contained in them that is discussed in the sentence in which the reference is relied upon.

In this specification and in the claims that follow, reference will be made to a number of terms, which shall be defined to have the following meanings:

20 Throughout the description and claims of this specification the word “comprise” and other forms of the word, such as “comprising” and “comprises,” means including but not limited to, and is not intended to exclude, for example, other additives, components, integers, or steps.

As used in the description and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a compound” includes mixtures of two or more such compounds, reference to “an ionic liquid” includes mixtures of two or more such ionic liquids, reference to “the film” includes mixtures of two or more such films, and the like.

30 “Optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event or circumstance occurs and instances where it does not.

Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly,

when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as "about" that particular value in addition to the value itself. For example, if the value "10" is disclosed, then "about 10" is also disclosed. It is also understood that when a value is disclosed that "less than or equal to" the value, "greater than or equal to the value" and possible ranges between values are also disclosed, as appropriately understood by the skilled artisan. For example, if the value "10" is disclosed, then "less than or equal to 10" as well as "greater than or equal to 10" is also disclosed. It is also understood that throughout the application data are provided in a number of different formats and that these data represent endpoints and starting points and ranges for any combination of the data points. For example, if a particular data point "10" and a particular data point "15" are disclosed, it is understood that greater than, greater than or equal to, less than, less than or equal to, and equal to 10 and 15 are considered disclosed as well as between 10 and 15. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

The term "nanomaterials" as used herein refers to compositions which contain one or more nanoparticulate substances along with a resin substrate material.

The term "resin substrate material(s)" as used herein includes one or more polymers, one or more copolymers, and combinations thereof.

The term "blend" as used herein, includes two or more polymers, two or more copolymers, and combinations thereof, immiscible or miscible at the molecular level or domain level.

The term "polymeric materials" includes one or more polymers, one or more copolymers, and combinations thereof.

The term "non-solvent" as used herein refers to a substance miscible with the one or more ionic liquids, but immiscible with the one or more resin substrate materials and the one or more nanoparticulate substances.

The term "substituted" as used herein is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, and

aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, for example, those described below. The permissible substituents can be one or more and the same or different for appropriate organic compounds. For purposes of this disclosure, the heteroatoms, such as nitrogen, can have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valences of the heteroatoms. This disclosure is not intended to be limited in any manner by the permissible substituents of organic compounds. Also, the terms "substitution" or "substituted with" include the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, *e.g.*, a compound that does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, etc.

A "residue" of a chemical species, as used in the specification and concluding claims, refers to the moiety that is the resulting product of the chemical species in a particular reaction scheme or subsequent formulation or chemical product, regardless of whether the moiety is actually obtained from the chemical species.

"A¹," "A²," "A³," and "A⁴" are used herein as generic symbols to represent various specific substituents. These symbols can be any substituent, not limited to those disclosed herein, and when they are defined to be certain substituents in one instance, they can, in another instance, be defined as some other substituents.

The term "alkyl" as used herein is a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, n-pentyl, isopentyl, s-pentyl, neopentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, eicosyl, tetracosyl, and the like. The alkyl group can also be substituted or unsubstituted. The alkyl group can be substituted with one or more groups including, but not limited to, substituted or unsubstituted alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, azide, nitro, silyl, sulfo-oxo, or thiol, as described herein. A "lower alkyl" group is an alkyl group containing from one to six carbon atoms.

The term "cycloalkyl" as used herein is a non-aromatic carbon-based ring composed of at least three carbon atoms. Examples of cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, norbornyl, and the like. The term "heterocycloalkyl" is a type of cycloalkyl group as defined above, and is included within the meaning of the term "cycloalkyl," where at least one of the carbon

atoms of the ring is replaced with a heteroatom such as, but not limited to, nitrogen, oxygen, sulfur, or phosphorus. The cycloalkyl group and heterocycloalkyl group can be substituted or unsubstituted. The cycloalkyl group and heterocycloalkyl group can be substituted with one or more groups including, but not limited to, substituted or
5 unsubstituted alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, azide, nitro, silyl, sulfo-oxo, or thiol as described herein.

The term "alkoxy" as used herein is an alkyl or cycloalkyl group bonded through an ether linkage; that is, an "alkoxy" group can be defined as —OA^1 where A^1 is alkyl or
10 cycloalkyl as defined above. "Alkoxy" also includes polymers of alkoxy groups as just described; that is, an alkoxy can be a polyether such as $\text{—OA}^1\text{—OA}^2$ or $\text{—OA}^1\text{—}(\text{OA}^2)_a\text{—OA}^3$, where "a" is an integer of from 1 to 200 and A^1 , A^2 , and A^3 are alkyl and/or cycloalkyl groups.

The term "alkenyl" as used herein is a hydrocarbon group of from 2 to 24 carbon
15 atoms with a structural formula containing at least one carbon-carbon double bond. Asymmetric structures such as $(\text{A}^1\text{A}^2)\text{C}=\text{C}(\text{A}^3\text{A}^4)$ are intended to include both the E and Z isomers. This may be presumed in structural formulae herein wherein an asymmetric alkene is present, or it may be explicitly indicated by the bond symbol $\text{C}=\text{C}$. The alkenyl group can be substituted with one or more groups including, but not limited to, substituted
20 or unsubstituted alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, azide, nitro, silyl, sulfo-oxo, or thiol, as described herein.

The term "cycloalkenyl" as used herein is a non-aromatic carbon-based ring composed of at least three carbon atoms and containing at least one carbon-carbon double
25 bound, *i.e.*, $\text{C}=\text{C}$. Examples of cycloalkenyl groups include, but are not limited to, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclopentadienyl, cyclohexenyl, cyclohexadienyl, norbornenyl, and the like. The term "heterocycloalkenyl" is a type of cycloalkenyl group as defined above, and is included within the meaning of the term "cycloalkenyl," where at least one of the carbon atoms of the ring is replaced with a
30 heteroatom such as, but not limited to, nitrogen, oxygen, sulfur, or phosphorus. The cycloalkenyl group and heterocycloalkenyl group can be substituted or unsubstituted. The cycloalkenyl group and heterocycloalkenyl group can be substituted with one or more groups including, but not limited to, substituted or unsubstituted alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, heteroaryl, aldehyde, amino,

carboxylic acid, ester, ether, halide, hydroxy, ketone, azide, nitro, silyl, sulfo-oxo, or thiol as described herein.

The term "alkynyl" as used herein is a hydrocarbon group of 2 to 24 carbon atoms with a structural formula containing at least one carbon-carbon triple bond. The alkynyl group can be unsubstituted or substituted with one or more groups including, but not limited to, substituted or unsubstituted alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, azide, nitro, silyl, sulfo-oxo, or thiol, as described herein.

The term "cycloalkynyl" as used herein is a non-aromatic carbon-based ring composed of at least seven carbon atoms and containing at least one carbon-carbon triple bond. Examples of cycloalkynyl groups include, but are not limited to, cycloheptynyl, cyclooctynyl, cyclononyl, and the like. The term "heterocycloalkynyl" is a type of cycloalkenyl group as defined above, and is included within the meaning of the term "cycloalkynyl," where at least one of the carbon atoms of the ring is replaced with a heteroatom such as, but not limited to, nitrogen, oxygen, sulfur, or phosphorus. The cycloalkynyl group and heterocycloalkynyl group can be substituted or unsubstituted. The cycloalkynyl group and heterocycloalkynyl group can be substituted with one or more groups including, but not limited to, substituted or unsubstituted alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, azide, nitro, silyl, sulfo-oxo, or thiol as described herein.

The term "aryl" as used herein is a group that contains any carbon-based aromatic group including, but not limited to, benzene, naphthalene, phenyl, biphenyl, phenoxybenzene, and the like. The term "aryl" also includes "heteroaryl," which is defined as a group that contains an aromatic group that has at least one heteroatom incorporated within the ring of the aromatic group. Examples of heteroatoms include, but are not limited to, nitrogen, oxygen, sulfur, and phosphorus. Likewise, the term "non-heteroaryl," which is also included in the term "aryl," defines a group that contains an aromatic group that does not contain a heteroatom. The aryl group can be substituted or unsubstituted. The aryl group can be substituted with one or more groups including, but not limited to, substituted or unsubstituted alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, boronic acid, ester, ether, halide, hydroxy, ketone, azide, nitro, hydroxamate, silyl, sulfo-oxo, or thiol as described herein. The term "biaryl" is a specific type of aryl group and is

included in the definition of “aryl.” Biaryl refers to two aryl groups that are bound together *via* a fused ring structure, as in naphthalene, or are attached *via* one or more carbon-carbon bonds, as in biphenyl.

The terms “amine” or “amino” as used herein are represented by the formula
 5 $NA^1A^2A^3$, where A^1 , A^2 , and A^3 can be, independently, hydrogen or substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein.

The term “boryl” as used herein is represented by the formula $\text{—}B(A^1)_2$, where
 10 A^1 can be hydroxyl, a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein. Also included within the meaning of this term are ionized compounds, salts, and tetravalent structures.

The term “carboxylic acid” as used herein is represented by the formula $\text{—}C(O)OH$. Throughout this specification “C(O)” is a short hand notation for a carbonyl
 15 group, *i.e.*, $C=O$.

The term “ester” as used herein is represented by the formula $\text{—}OC(O)A^1$ or $\text{—}C(O)OA^1$, where A^1 can be a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein. The
 20 term “polyester” as used herein is represented by the formula $\text{—}(A^1O(O)C-A^2-C(O)O)_a\text{—}$ or $\text{—}(A^1O(O)C-A^2-OC(O))_a\text{—}$, where A^1 and A^2 can be, independently, a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group described herein and “a” is an interger from 1 to 500. “Polyester” is as the term used to describe a group that is produced by the reaction between a compound having at least two carboxylic acid groups with a compound having at least two hydroxyl
 25 groups.

The term “ether” as used herein is represented by the formula A^1OA^2 , where A^1 and A^2 can be, independently, a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group described herein. The term
 “polyether” as used herein is represented by the formula $\text{—}(A^1O-A^2O)_a\text{—}$, where A^1 and
 30 A^2 can be, independently, a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group described herein and “a” is an integer of from 1 to 500. Examples of polyether groups include polyethylene oxide, polypropylene oxide, and polybutylene oxide.

The term “halide” as used herein refers to the halogens fluorine, chlorine,

bromine, and iodine.

The term "hydroxyl" as used herein is represented by the formula —OH .

The term "ketone" as used herein is represented by the formula $\text{A}^1\text{C(O)A}^2$, where A^1 and A^2 can be, independently, a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein.

The term "azide" as used herein is represented by the formula —N_3 .

The term "nitro" as used herein is represented by the formula —NO_2 .

The term "nitrile" as used herein is represented by the formula —CN .

The term "silyl" as used herein is represented by the formula $\text{—SiA}^1\text{A}^2\text{A}^3$, where A^1 , A^2 , and A^3 can be, independently, hydrogen or a substituted or unsubstituted alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein.

The term "sulfo-oxo" as used herein is represented by the formulas —S(O)A^1 , $\text{—S(O)}_2\text{A}^1$, $\text{—OS(O)}_2\text{A}^1$, or $\text{—OS(O)}_2\text{OA}^1$, where A^1 can be hydrogen or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein. Throughout this specification "S(O)" is a short hand notation for S=O . The term "sulfonyl" is used herein to refer to the sulfo-oxo group represented by the formula $\text{—S(O)}_2\text{A}^1$, where A^1 can be hydrogen or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein. The term "sulfone" as used herein is represented by the formula $\text{A}^1\text{S(O)}_2\text{A}^2$, where A^1 and A^2 can be, independently, a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein. The term "sulfoxide" as used herein is represented by the formula $\text{A}^1\text{S(O)A}^2$, where A^1 and A^2 can be, independently, a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein.

The term "thiol" as used herein is represented by the formula —SH .

Reference will now be made in detail to specific aspects of the disclosed materials, compounds, compositions, articles, and methods, examples of which are illustrated in the accompanying Examples.

Certain materials, compounds, compositions, and components disclosed herein can be obtained commercially or readily synthesized using techniques generally known to those of skill in the art. For example, the starting materials and reagents used in preparing the disclosed compounds and compositions are either available from commercial

suppliers such as Aldrich Chemical Co., (Milwaukee, Wis.), Acros Organics (Morris Plains, N.J.), Fisher Scientific (Pittsburgh, Pa.), or Sigma (St. Louis, Mo.) or are prepared by methods known to those skilled in the art following procedures set forth in references such as Fieser and Fieser's Reagents for Organic Synthesis, Volumes 1-17 (John Wiley and Sons, 1991); Rodd's Chemistry of Carbon Compounds, Volumes 1-5 and
5 Supplementals (Elsevier Science Publishers, 1989); Organic Reactions, Volumes 1-40 (John Wiley and Sons, 1991); March's Advanced Organic Chemistry, (John Wiley and Sons, 4th Edition); and Larock's Comprehensive Organic Transformations (VCH Publishers Inc., 1989).

10 Also, disclosed herein are materials, compounds, compositions, and components that can be used for, can be used in conjunction with, can be used in preparation for, or are products of the disclosed methods and compositions. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various
15 individual and collective combinations and permutation of these compounds may not be explicitly disclosed, each is specifically contemplated and described herein. For example, if a compound is disclosed and a number of modifications that can be made to a number of components of the compound are discussed, each and every combination and permutation that are possible are specifically contemplated unless specifically indicated to
20 the contrary. Thus, if a class of components A, B, and C are disclosed as well as a class of components D, E, and F and an example of a combination compound A-D is disclosed, then even if each is not individually recited, each is individually and collectively contemplated. Thus, in this example, each of the combinations A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are specifically contemplated and should be considered disclosed from
25 disclosure of A, B, and C; D, E, and F; and the example combination A-D. Likewise, any subset or combination of these is also specifically contemplated and disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E are specifically contemplated and should be considered disclosed from disclosure of A, B, and C; D, E, and F; and the example combination A-D. This concept applies to all aspects of this disclosure including, but not
30 limited to, steps in methods of making and using the disclosed compositions. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific aspect or combination of aspects of the disclosed methods, and that each such combination is specifically contemplated and should be considered disclosed.

Disclosed herein is process comprising dissolving and/or suspending one or more resin substrate materials and one or more magnetic nanoparticulate substances in a medium comprising one or more ionic liquids to provide a mixture, and recovering a solid nanomaterial comprising the one or more resin substrate materials having the one or more magnetic nanoparticulate substances distributed therein by combining the mixture with a substance miscible with said one or more ionic liquids, but immiscible with said one or more resin substrate materials and said one or more nanoparticulate substances, wherein during said recovery step, an electromagnetic field is applied to the mixture to align said one or more nanoparticulate substances within said one or more resin substrate materials; and the nanomaterials produced thereby, along with their use in providing information storage media such as smart paper and magnetic recording tape.

Ionic liquids are a well-established class of liquids containing solely ionized species, and having melting points largely below 150°C, or most preferably below 100°C. In most cases, ionic liquids (ILs) are organic salts containing one or more cations that are typically ammonium, imidazolium, or pyridinium ions, although many other types are known.

Disclosed herein are processes for the production of nanomaterials in which the nanoparticles are aligned and substantially uniformly distributed within the resin substrate material. The process comprises dissolving and/or suspending one or more resin substrate materials and one or more magnetic nanoparticulate substances in a medium comprising one or more ionic liquids to provide a mixture, and recovering a solid nanomaterial comprising the one or more resin substrate materials having the one or more magnetic nanoparticulate substances distributed therein by combining the mixture with a non-solvent, wherein during the recovery step, an electromagnetic field is applied to the mixture to align the one or more nanoparticulate substances within the one or more resin substrate materials.

The unique solvation properties of ionic liquids allow for the dissolution of a wide range of resin substrate materials, particularly materials useful in the production of magnetic information storage media, such as polyesters and cellulose materials. Further, these unique solvation properties also allow the ionic liquid to dissolve a wide range of magnetic nanoparticulate substances. This dual dissolution ability permits intimate mixing of the resin substrate materials and the magnetic nanoparticulate substances, which, upon adding the mixture to a “non-solvent” in turn, allows for the creation of nanomaterials, most preferably in the form of sheets or films, wherein the magnetic

nanoparticulate substances are distributed throughout the resin substrate material and are aligned due to the presence of the electromagnetic field during the reconstitution step during which the nanoparticles are still mobile and alignable. The resulting nanomaterials can be in any desired form, *e.g.*, in the form of sheets or films, suitable for the creation of information storage media, due to the high anisotropy and alignment of the nanoparticles within the resin substrate material. These information storage media can be recorded using any conventional recording force used for the particular type of recording medium, such as electrical, magnetic, light, heat, etc. Suitable information storage media include, but are not limited to, materials known as "smart paper" (also known in the art as e-ink, reusable sign media or e-paper; such as the electronic-display technology based on full-color programmable media produced by Magink, from Neveh-Ilan, Israel) and in magnetic storage tapes or disks.

Suitable non-solvents include, but are not limited to, polar liquid systems, such as water, alcohols, and other hydric liquids. In one example, the ionic liquid is removed by the addition of water.

The magnetic field used can be uniaxial, biaxial, or triaxial, depending on the type of orientation of the nanoparticles desired, and is applied to the resin substrate material containing nanoparticles in accordance with methods well known in the art. The magnetic field used to align the nanoparticulate materials can have any desired field strength, for example, in a range of from about 10 to about 1000 Gauss, or from about 50 to about 350 Gauss.

The processes disclosed herein can use polymers that contain various repeating monomeric units as the resin substrate material. These monomer units can contain polar, non-ionic, and charged groups, including, but not limited to, $-\text{NH}_2$ -, $-\text{NHR}$ -, $-\text{NR}_2$ -, $-\text{N}^+\text{R}_3\text{X}^-$, $-\text{O}-$, $-\text{OH}$ -, $-\text{COOH}$ -, $-\text{COO}^-\text{M}^+$ -, $-\text{SH}$ -, $-\text{SO}_3\text{M}^+$ -, $-\text{PO}_3^{2-}\text{M}^{2+}$ -, $-\text{PR}_3$ -, $-\text{NH}-\text{CO}-\text{NH}_2$ and $-\text{NHC}(\text{NH})\text{NH}_2$. These groups may be present in sufficient numbers along, or pendent to, the polymeric backbone, in polymers, such as, polyacrylamide, polyvinyl alcohol, polyvinyl acetate, polyamides, polyesters, polyimideamides, polybenzimidazole, aramides, polyimides, poly(*N*-vinylpyrrolidinone), and poly(hydroxyethyl acrylate).

These groups also impact the solubility of the respective polymer. The polymer can have a complex structure due to intramolecular hydrogen bonding, ionic interactions, intermolecular interactions, and chain-chain complexation. These interactions govern the solution properties and performance.

Solvent properties such as polarity, charge, hydrogen bonding, interactions

between the polymer and the solvent can also be considered for effective dissolution and blending.

Three abundant polysaccharides, cellulose, starch, and chitin, do not dissolve in most common solvents directly due to their unique molecular and supermolecular structure. One way to enhance a polymer's dissolution is to chemically modify it, for example, by adding one or more hydroxyethyl, hydroxypropyl, methyl, carboxymethyl, sulfate, or phosphate groups to the polymer structure. These modifications alter the polymer's aforementioned interactions and can thereby increase its solubility in common organic solvents and in many cases water. Instead of chemically altering the polymer, the disclosed methods provides a method of processing the virgin polymer using ionic liquids as the solvent, thus lessening chemical usage and processing steps and making the overall process more environmentally and economically sustainable. It is contemplated, however, that polymers modified as described can also be used in the disclosed methods. The use of cellulose, in particular, is useful in the production of smart papers, which can store information and can be reused upon re-recording of the information on the paper.

Ionic Liquids ("ILs") have a more complex solvent behavior compared with traditional aqueous and organic solvent, because ILs are salts and not a molecular, nonionic solvent. Types of interactions between ILs with many solutes include dispersion, π - π , σ - π , hydrogen bonding, dipolar and ionic/charge-charge. The Abraham solvation equation is a useful method used to characterize ILs solvent property to understand the polymer dissolution behavior in ILs. Some typical C₄mim ILs interaction parameters are shown in Table 1 below. ILs that have strong dipolarity, hydrogen bond accepting (A) ability, and hydrogen bond donating (B) ability are compared with other solvents that are capable of dissolving cellulose (*see table below*). C₄mim C1, one of the most unique solvents, shows the largest A ($a = 4.860$) and a strong ability to interact with solute molecules *via* non-bonding or π -electron interaction ($r = 0.408$). The cation C₄mim, in combination with the anion C1⁻, exhibits significant ability to interact with π -systems of solute molecules (*Anderson, J.L. et al*). The smaller Gibbs free energies of hydration of Cl ($\Delta G_{\text{hyd}} = -347$ kJ/mol) shows a larger HBA 4.860, compared to that of 1.660 of [BF₄⁻] ($\Delta G_{\text{hyd}} = -200$ kJ/mol).

Table 1					
Ionic liquid	excess	Polarity /	hydrogen	hydrogen	molecular

	molecular refraction	polarisability parameter	bond acidity parameter	bond basicity parameter	volume
C ₄ mim Cl	0.408	1.826	4.860	-0.121	0.392
C ₄ mim BF ₄	-0.141	1.365	1.660	-0.283	0.473
C ₄ mim PF ₆	0	1.540	1.369	0	0.439
Dimethylacetamide	0.36	1.33	0	0.78	0.787
Dimethylformamide	0.37	1.31	0	0.74	0.6468
Dimethylsulfoxide	0.52	1.74	0	0.88	0.776

In some examples, the disclosed processes provide the mixing of one or more resin substrate materials (polymers and/or copolymers) and one or more magnetic nanoparticulate substances with one or more ionic liquids. Mixing can be accomplished by any conventional procedure in the art, including, but not limited to, various stirring mechanisms, agitation mechanisms, sonication, and vortexing. In one specific example, the mixture is heated to about 100°C. The addition of heat can be supplied by any conventional and non-conventional heat source, including, but not limited to, a microwave source. It has been found that microwave radiation not only provides heat but also facilitates the dissolution of polymeric materials in the ionic liquid. While not wishing to be bound by theory, it is believed that the facilitated dissolution can be due to the absorption and resulting increase molecular motions of solute and solvent.

In other examples wherein the resin substrate material is cellulose, ionic liquids can allow for the dissolution of cellulose without derivatization in high concentration. Such a solution can be heated to about 100°C, or to about 80°C, in an ultrasonic bath. This heating can be effectively accomplished by using microwave radiation supplied by a domestic microwave oven. In one example, an admixture of hydrophilic ionic liquid and cellulose is heated to a temperature of from about 100°C to about 150°C using microwave radiation. Further methods for dissolution of cellulose in ionic liquids are described in U.S. Patent No. 6,824,599 and 6,808,557, which are incorporated by reference herein in their entireties for their teachings of ionic liquids and methods for using them.

Resin Substrate Materials

Suitable resin substrate materials for use in the process of the present invention include, but are not limited to, polymers and copolymers formed by step, chain, ionic,

ring-opening, and catalyzed polymerizations.

Suitable polymers and copolymers can be derived from natural and synthetic sources including, but not limited to, polysaccharides, polyester, polyamide, polyurethane, polysiloxane, phenol polymers, polysulfide, polyacetal, polyolefins, acrylates, methacrylates and dienes. In particular, preferred polymers include, but are not limited to, cellulose, hemicellulose, starch, chitin, silk, wool, poly-2-hydroxymethylmethacrylate, poly-2-hydroxyethylmethacrylate, polyamides, polyesters, polyimideamides, polybenzimidazole, aramides, polyimides, polyvinyl alcohol, polyaniline, polyethylene glycol, polyacrylonitrile, polystyrene, polyethylene oxide with terminal amine groups, linear polyethyleneimine, and branched polyethyleneimine.

Monomers include, but are not limited to, α -olefins, 2-hydroxyalkylmethacrylate, aniline, acrylonitrile, ethylene, isobutylene, styrene, vinyl chloride, vinyl acetate, vinyl alcohol, methyl methacrylate, ethylene glycol, cellobiose, vinylidene chloride, tetrafluoroethylene, formaldehyde, acetaldehyde, vinylpyrrolidinone, butadiene, and isoprene.

Magnetic Nanoparticulate Substances

The magnetic nanoparticulate substances suitable for the disclosed methods and compositions can be any magnetic material having nanoscale dimensions that is susceptible of alignment or orientation in the presence of an electromagnetic field. Suitable magnetic nanoparticulate substances include, but are not limited to, iron, cobalt, nickel, oxides thereof and mixtures/alloys thereof. Further examples of magnetic nanoparticulate substances include one or more of cobalt particles, iron-cobalt particles, iron oxide particles, nickel particles, and mixtures thereof.

Ionic Liquids

The ionic liquids comprise one or more cations and one or more anions. In many examples, a mixture of cations and anions is selected and optimized for the dissolution of a particular combination of one or more resin substrate materials and one or more magnetic nanoparticulate materials.

In other examples, the cation is derived from an organic compound including, but not limited to, the following heterocyclics: imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiazoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophenes, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophenes, dibenzothiophenes, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines,

phthalazines, quinazolines and quinoxalines, quinolines, pyrrolidines, isoquinolines, and combinations thereof.

The anionic portion of the ionic liquid can comprise at least one of the following groups: halogens, BX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , BR_4^- , substituted or unsubstituted carboranes, substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, substituted or unsubstituted carboxylates, triflates and noncoordinating anions; and wherein R is at least one member selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

In other examples, cations that contain a single five-membered ring free of fusion to other ring structures, such as an imidazolium cation, are suitable, and the anion of the ionic liquid can be a halogen or pseudohalogen. For example, a 1,3-di-($\text{C}_1\text{--C}_6$ alkyl or $\text{C}_1\text{--C}_6$ alkoxyalkyl)-substituted-imidazolium ion is a suitable cation. The corresponding anion can be a halogen or pseudohalogen. In addition, a 1-($\text{C}_1\text{--C}_6$ alkyl)-3-(methyl)-imidazolium [C_nmim , where $n = 1\text{--}6$] cation is also suitable, and a halogen is a suitable anion.

Further examples of ionic liquid are ones that are liquid at or below a temperature of about 200°C (e.g., below a temperature of about 150°C) and above a temperature of about -100°C . For example, *N*-alkylisoquinolinium and *N*-alkylquinolinium halide salts have melting points of less than about 200°C . The melting point of *N*-methylisoquinolinium chloride is about 183°C , and *N*-ethylquinolinium iodide has a melting point of about 158°C . In other examples, a contemplated ionic liquid is liquid (molten) at or below a temperature of about 120°C and above a temperature of minus 44°C . Still further, a contemplated ionic liquid is liquid (molten) at a temperature of about minus 10°C to about 100°C .

Further examples of ionic liquids include, but are not limited to, [C_2mim]Cl, [C_3mim]Cl, [C_4mim]Cl, [C_6mim]Cl, [C_8mim]Cl, [C_2mim]I, [C_4mim]I, [C_4mim][PF_6], [C_2mim][PF_6], [C_3mim][PF_6], [C_3mim][PF_6], [C_6mim][PF_6], [C_4mim][BF_4], [C_2mim][BF_4], [C_2mim][$\text{C}_2\text{H}_3\text{O}_2$], and [C_2mim][$\text{C}_2\text{F}_3\text{O}_2$].

Illustrative 1-alkyl-3-methyl-imidazolium ionic liquids, [$\text{C}_n\text{--mim}$]X, where $n = 4$ and 6, $\text{X} = \text{Cl}^-$, Br^- , SCN^- , $(\text{PF}_6)^-$, $(\text{BF}_4)^-$, and [C_8mim]Cl have been prepared. The dissolution of cellulose (fibrous cellulose, from Aldrich Chemical Co.) in those

illustrative ionic liquids under ambient conditions with heating to 100°C, with sonication and with microwave heating, has been examined. Dissolution is enhanced by the use of microwave heating. Cellulose solutions can be prepared very quickly, which is energy efficient and provides associated economic benefits.

5 In one example of an ionic liquids and a solution prepared from such a liquid is substantially free of water or a nitrogen-containing base. Such a liquid or solution contains about one percent or less of water or a nitrogen-containing base. Thus, when a solution is prepared, it is prepared by admixing the ionic liquid and cellulose in the absence of water or a nitrogen-containing base to form an admixture.

10 A range of different cations can be employed of those screened from the common sets used to prepare ionic liquids; imidazolium salts appear to be most effective, with the smallest imidazolium cation exhibiting the easiest dissolution. Alkyl-pyridinium salts free of organic base were somewhat less effective. Smaller phosphonium and ammonium quaternary salts containing shorter chain alkyl substituents are known, but have higher
15 melting points and are often not liquid within the acceptable range for definition as ionic liquids.

The use of an imidazolium chloride ionic liquid as solvent for cellulose provides a significant improvement over the previously-reported solubility of cellulose in the organic salt/base *N*-benzylpyridinium chloride/pyridine as discussed in U.S. Patent 1,943,176, and
20 in which the maximum solubility was 5 weight percent. Indeed, additional nitrogen-containing bases as were used in that patent are not required to obtain good solubility of cellulose in the ionic liquids.

Other ionic liquids include, but are not limited to, those ionic liquids disclosed in U.S. Patent 6,824,599 and U.S. Patent 6,808,557, the contents of each being hereby
25 incorporated by reference in their entirety for at least their teaching of ionic liquids.

Additives

Any conventional additive used in polymeric formulations can be incorporated into the nanomaterials of compositions and methods disclosed herein. If these additives are incorporated during the dissolution stage of the resin substrate materials and magnetic
30 nanoparticulate substances, such additives should not interfere with the solute-solvent and solvent-solvent interactions. Examples of conventional additives include, but are not limited, plasticizers, fillers, colorants, UV-screening-agents and antioxidants. Other additives include, but are not limited to, those additives disclosed in U.S. Patent 6,808,557.

EXAMPLES

The following examples are set forth below to illustrate the methods and results according to the disclosed subject matter. These examples are not intended to be inclusive of all aspects of the subject matter disclosed herein, but rather to illustrate
5 representative methods and results. These examples are not intended to exclude equivalents and variations of the present invention which are apparent to one skilled in the art.

Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.) but some errors and deviations should be accounted for.

- 10 Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric. There are numerous variations and combinations of reaction conditions, *e.g.*, component concentrations, desired solvents, solvent mixtures, temperatures, pressures and other reaction ranges and conditions that can be used to optimize the product purity and yield obtained from the described process.
- 15 Only reasonable and routine experimentation will be required to optimize such process conditions.

Example 1:

- As an example of the operation of the disclosed processes, the nanoparticles are suspended in a mixture of the ionic liquid and the resin substrate material, *e.g.*, dissolved
20 cellulose. The nanoparticles are present in a range of from 2.0 to 30.0 wt% relative to ionic liquid. The resin substrate material is present in an amount of from 2 to 20 wt% relative to ionic liquid. The obtained suspension is placed in an ultrasonic bath for 1 hour, then degassed in a vacuum oven (*e.g.*, at about 50°C for approximately 10 minutes). A 150 Gauss magnetic field is then supplied using a single magnetic field source or a
25 combination of magnetic field sources. The resin substrate material is reconstituted with the nanoparticles captured therein in an aligned configuration, by contacting with water to remove the ionic liquid while causing the resin substrate material to reconstitute in solid form with the nanoparticles encapsulated therein, all while maintaining the presence of the magnetic field. The contacting with water can be performed by a variety of methods,
30 such as extrusion of the mixture in the form of a sheet into water, casting the mixture into a sheet and washing the sheet with water to remove the ionic liquid.

In preferred method for performing the present invention, the mixture is manually homogenized (to ensure complete mutual dispersion) and then cast as a film (approximately 1 mm thickness) on a glass plate using coating rods (R&D Specialties,

Weber, NY). The films are reconstituted and the IL solvent is leached from the films with deionized (DI) H₂O. Following complete reconstitution, the film is placed in a bath and immersed in DI H₂O for at least 24 hours to leach residual IL (such as [C₄mim]Cl) from the film.

5 Other advantages which are obvious and which are inherent to the invention will be evident to one skilled in the art. It will be understood that certain features and sub-combinations are of utility and may be employed without reference to other features and sub-combinations. This is contemplated by and is within the scope of the claims. Since many possible embodiments may be made of the invention without departing from the
10 scope thereof, it is to be understood that all matter herein set forth or shown in the accompanying drawings is to be interpreted as illustrative and not in a limiting sense.

CLAIMS

What is claimed is:

1. A method for making a nanomaterial, comprising:
 - a. dissolving and/or suspending a combination of (i) one or more resin substrate materials and (ii) one or more magnetic nanoparticulate substances in a medium comprising one or more ionic liquids, to provide a mixture; and
 - b. recovering a solid nanomaterial comprising the one or more resin substrate materials having the one or more magnetic nanoparticulate substances distributed therein, by combining the mixture with a non-solvent; wherein during the recovery step, an electromagnetic field is applied to the mixture to align the one or more nanoparticulate substances within the one or more resin substrate materials.
2. The method of claim 1, wherein the electromagnetic field is a uniaxial electromagnetic field.
3. The method of claim 1, wherein the electromagnetic field is a biaxial electromagnetic field.
4. The method of claim 1, wherein the electromagnetic field is a triaxial electromagnetic field.
5. The method of claim 1, wherein the one or more resin substrate materials are at least one member selected from the group consisting of polysaccharides, polyesters, polyamides, polyurethanes, polysiloxanes, phenol polymers, polysulfides, polyacetals, polyolefins, acrylates, methacrylates, polyamides, polyesters, polyimideamides, polybenzimidazole, aramides, polyimides, and dienes.
6. The method of claim 5, wherein the one or more resin substrate materials comprises cellulose or a derivative thereof.
7. The method of claim 1, wherein the medium comprises one or more ionic liquids having a cation portion of the one or more ionic liquids formed from at least one member selected from the group consisting of imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiazoles, triazoles, selenozoles, oxaphospholes, pyrroles,

boroles, furans, thiophenes, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophenes, dibenzothiophenes, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines, quinolines, pyrrolidines, isoquinolines, and combinations thereof.

8. The method of claim 1, wherein the medium comprises one or more ionic liquids having an anionic portion of the one or more ionic liquids formed from at least one member selected from the group consisting of halogens, BX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , BR_4^- , carboranes, substituted carboranes, metallocarboranes, substituted metallocarboranes, phosphates, phosphites, polyoxometallates, carboxylates, substituted carboxylates, triflates and noncoordinating anions; wherein R is at least one member selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.
9. The method of claim 1, wherein the medium comprises one or more ionic liquids selected from the group consisting of $[\text{C}_2\text{mim}]\text{Cl}$, $[\text{C}_3\text{mim}]\text{Cl}$, $[\text{C}_4\text{mim}]\text{Cl}$, $[\text{C}_6\text{mim}]\text{Cl}$, $[\text{C}_8\text{mim}]\text{Cl}$, $[\text{C}_2\text{mim}]\text{I}$, $[\text{C}_4\text{mim}]\text{I}$, $[\text{C}_4\text{mim}][\text{PF}_6]$, $[\text{C}_2\text{mim}][\text{PF}_6]$, $[\text{iC}_3\text{mim}][\text{PF}_6]$, $[\text{C}_6\text{mim}][\text{PF}_6]$, $[\text{C}_6\text{mim}][\text{PF}_6]$, $[\text{C}_4\text{mim}][\text{BF}_4]$, $[\text{C}_2\text{mim}][\text{BF}_4]$, $[\text{C}_2\text{mim}][\text{C}_2\text{H}_3\text{O}_2]$, and $[\text{C}_2\text{mim}][\text{C}_2\text{F}_3\text{O}_2]$.
10. The method of claim 1, wherein the non-solvent is a member selected from the group consisting of water and alcohols.
11. The method of claim 1, wherein the one or more magnetic nanoparticulate substances are at least one member selected from the group consisting of iron, cobalt, nickel, oxides thereof, alloys thereof and mixtures thereof.
12. An information storage medium, comprising a matrix of one or more resin substrate materials, having distributed therethrough one or more magnetic nanoparticulate substances, wherein the one or more magnetic nanoparticulate

substances is aligned within said matrix and susceptible to change in orientation in response to application of a recording force.

13. The information storage medium of claim 12, wherein the information storage medium is in a form of a sheet, a film, or a disk.
14. A nanomaterial prepared by the method of claim 1.
15. The nanomaterial of claim 14, wherein the nanomaterial is in a form of a sheet or film.